Ethylbenzene from Polystyrene Waste as Aromatic Additive for SAF

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ILLINOIS

Background and challenges

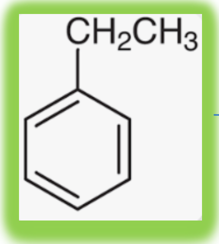
- Jet fuel contributed about **14%** of all transportation sector emissions (2022).
- Sustainable Aviation Fuel (SAF) Grand Challenge aims to curb aviation emissions by expanding the production of domestic sustainable aviation fuel to **3 billion gallons per year by 2030** and **100% of projected aviation jet fuel use, or 35 billion gallons per year by 2050.**
- Hydrotreated Ester and Fatty Acid (HEFA) lacks aromatics; A minimum of 8 vol. % aromatics required.
- Blending restricted to <50 vol. % by law.
- In reality, most commercial blends are 30/70 blends of Synthetic Paraffinic Kerosene (SPK) and Jet Fuel.

Image courtesy of https://www.energy.gov/eere/bioenergy/articles/sustainable-aviation-fuel-grand-challenge-roadmap-flight-plan-sustainable

Opportunity

- About 2.5 million metric tons polystyrene (#6) produced in the United States in 2019.

Oil



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SPK

Enhanced SPK

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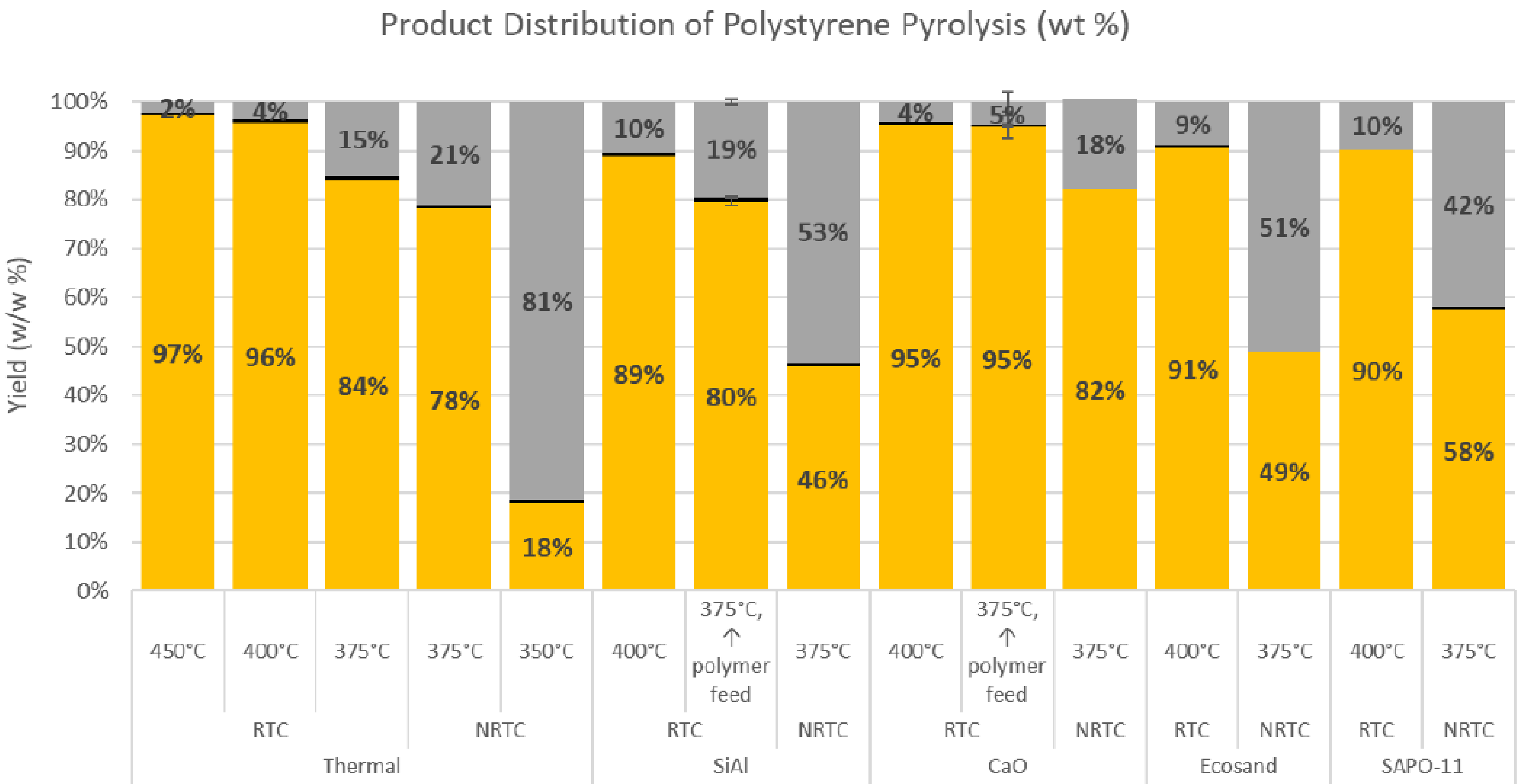
Jet fuel

- More SPK can be added with jet fuel.

Image generated via canva.com

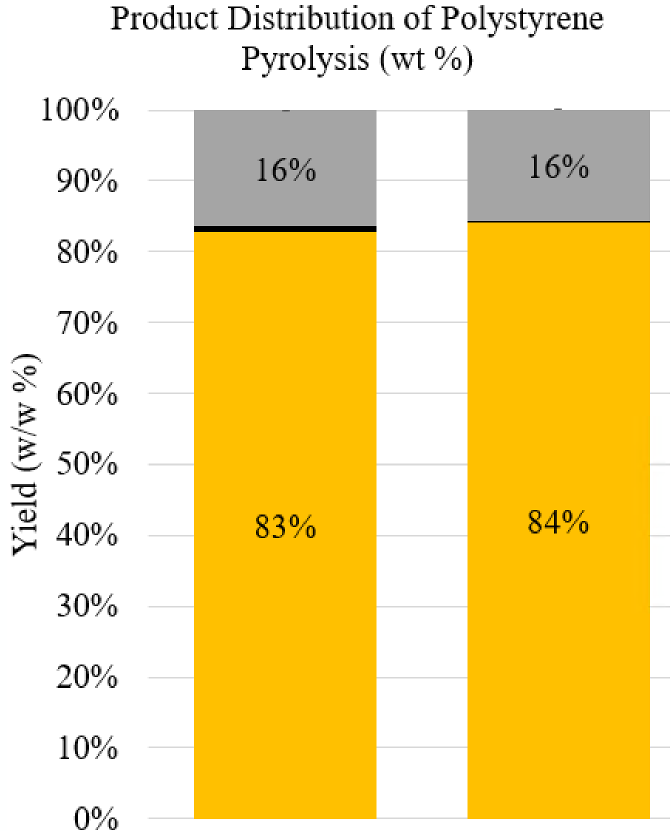
PS to oil



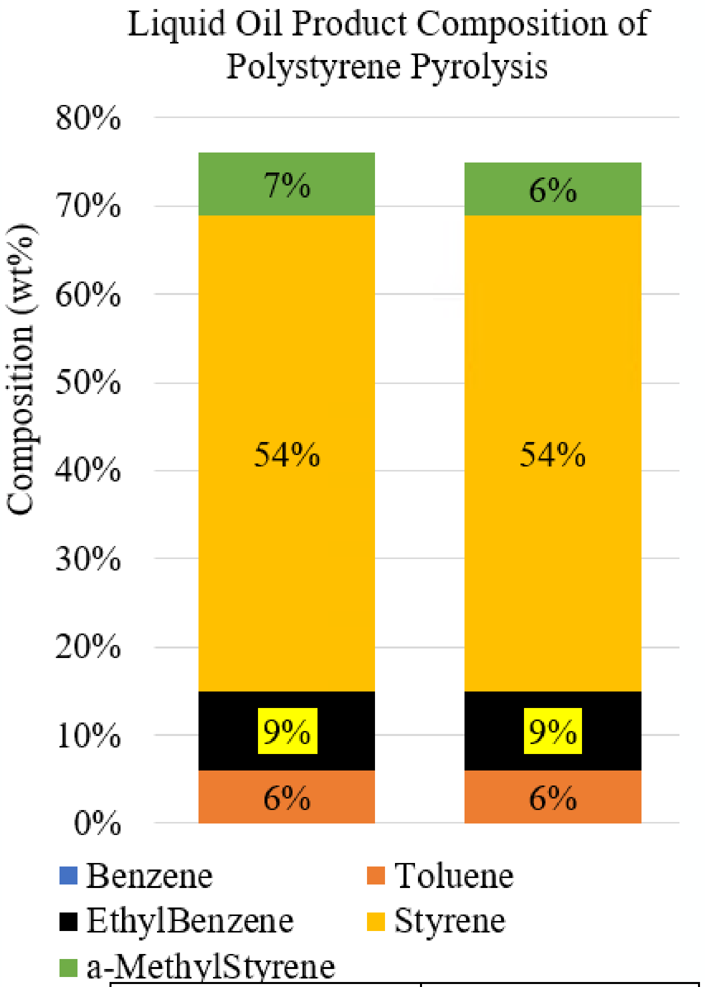
	Thermal					SiAl			CaO			Ecosand		SAPO-11	
	RTC			NRTC		RTC		NRTC	RTC		NRTC	RTC	NRTC	RTC	NRTC
	450°C	400°C	375°C	375°C	350°C	400°C	375°C, ↑ polymer feed	375°C	400°C	375°C, ↑ polymer feed	375°C	400°C	375°C	400°C	375°C
Solids	2%	4%	15%	21%	81%	10%	19%	53%	4%	5%	18%	9%	51%	10%	42%
Gas	0%	1%	1%	1%	1%	1%	1%	1%	1%	0%	0%	0%	0%	0%	0%
Liquid Oil	97%	96%	84%	78%	18%	89%	80%	46%	95%	95%	82%	91%	49%	90%	58%

- PS 1200 with and without catalysts compared using 100 g/batch reactor
- PS decomposed readily to produce liquid crude oil products

Waste PS to oil: yield and composition



	400 °C, RTC, Thermal	400 °C, RTC, CaO
Solids	16%	16%
Gas	1%	0%
Liquid Oil	83%	84%



400 °C, RTC, Thermal	400 °C, RTC, CaO

PS oil upgradation: hydrogenation with Pd/C

Feed	Catalyst	T, P	Benzene	Toluene	Ethylbenzene	Styrene	α-Methyl styrene	1,2-Diphenyl propane	Styrene Dimer	Styrene Trimer
PS crude oil	(Thermal)	400 °C	0	3	2	57	5	5	13	4
Hydrogenated PS oil	Pd/C	160 °C 60 bar	0	3	55	0	0	6	0	0
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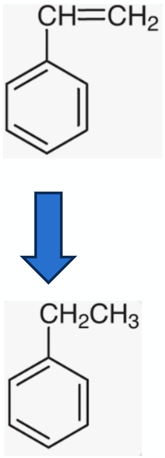
Feed	Catalyst	T, P	Benzene	Toluene	Ethylbenzene	Styrene	α-Methyl styrene	1,2-Diphenyl propane	Styrene Dimer	Styrene Trimer
PS crude oil	(Thermal)	400 °C	0	2	1	55	4	5	15	6
Hydrogenated PS oil	Pd/C	70 °C 55 bar	0	2	53	0	0	0	0	0



- Styrene dominated in crude oil
- Hydrogenation of styrene to EB: >96% conversion

Hydrogenated PS oil: separation of EB

#	Temp (°C)	wt %	Benzene	Toluene	Ethylbenzene	Styrene	α-Methyl styrene	1,2-Diphenyl propane	Styrene Dimer	Styrene Trimer
Hydrogenated PS oil			0	3	49	0	0	8	0	0
Distillate cut (52b)	<131°C	10.5	0	29	64	0	0	0	0	0
Distillate cut (53b)	131-141°C	43.5	0	3	89	0	0	0	0	0
Distillate cut (54b)	>151°C	45.3	0	0	0	0	0	18	0	0

- EB dominated in hydrogenated oil
- High purity EB can be obtained within a T window of 131-141 °C

Blending EB with HEFA: property change

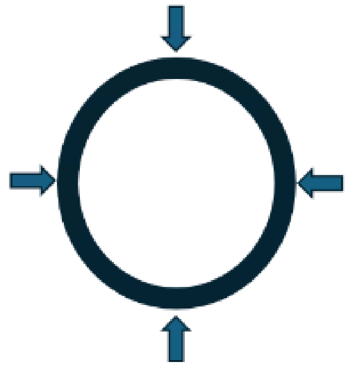
- Base fuel: HEFA-SPK (AltAir Paramount Aviation Turbine Fuel, Courtesy of World Energy LLC).
- Property changes within expect with addition of EB.

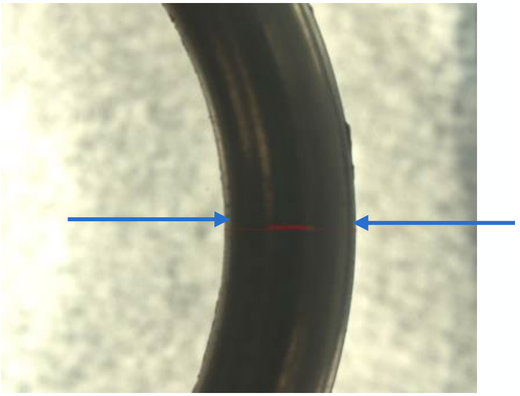
Description of sample	Additive	FP	AV	Moisture	Density at 15°C	KV at -20°C	KV at 40°C	Lubricity at 60°C	IP	Oxidative stability	HHV
	Vol. %	°C	mg KOH/g	ppm	kg/m^3	mm^2/s	mm^2/s	micron	h	°C	MJ/kg
ASTM D7566-22		< -40	<0.1		775-840	<8.0		<850			
HEFA	0	-73.7	0.19	49	744	2.88	1.04	582	89.0	199.8	47.2
HEFA w/ Comm. EB	4	-76.0	0.10	33	749	2.61	0.96	709	67.4		47.1
HEFA w/ Comm. EB	8	-76.1	0.10	41	754	2.46	0.93	761	59.7		46.9
HEFA w/ Comm. EB	12	-76.1	0.15	45	758	2.46	0.95	720	66.8		46.7
HEFA w/ Comm. EB	16	-79.2	0.34	27	764	2.19	0.87	775	56.0	202.8	46.5
HEFA w/ PS EB fraction	12	-79.0	0.21	16	759	2.33	0.90	726	/	201.3	46.7
HEFA w/ PS EB fraction	16	-79.1	0.32	21	764	2.16	0.85	721	/	202.6	46.5

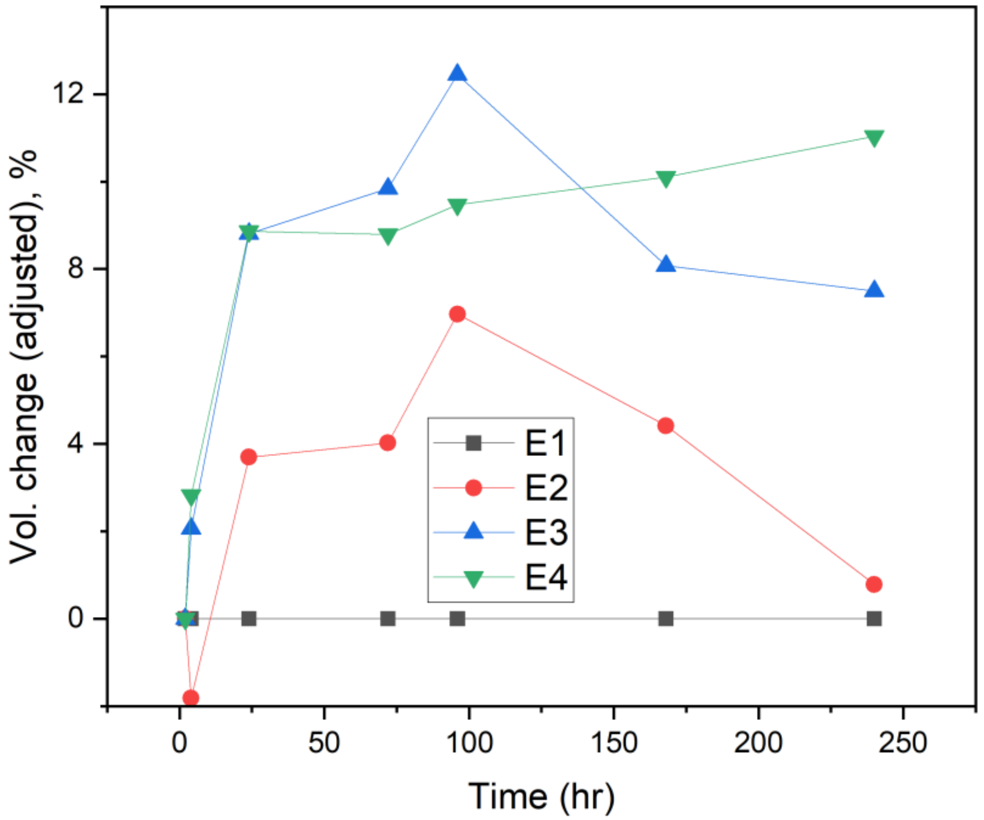
Blending EB with HEFA: O-ring swelling improvement

- O-ring: Durometer 70A Buna-N (ID ½”, OD 5/8”)

Sample #	Additive	Con.
E1	No	
E2	PS EB fraction	12 vol. %
E3	PS EB fraction	16 vol. %
E4	Commercial EB	16 vol. %

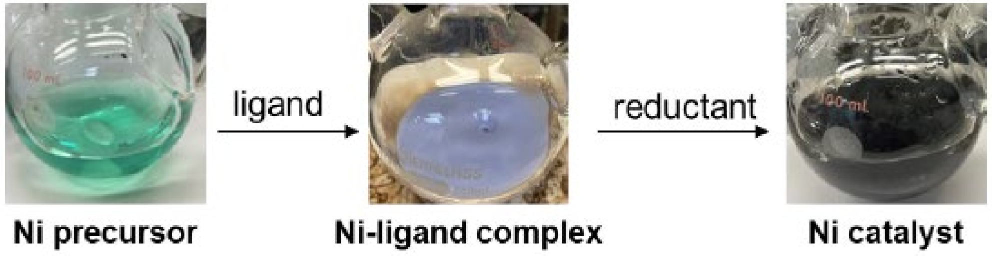




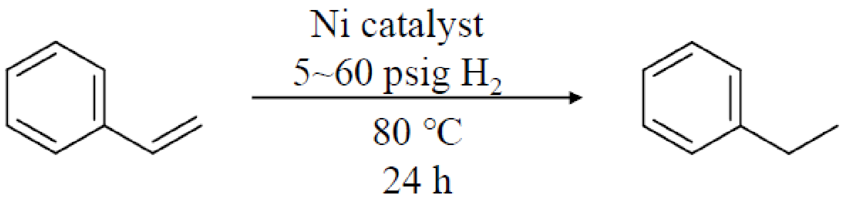


Recent findings on hydrogenation

- Ni

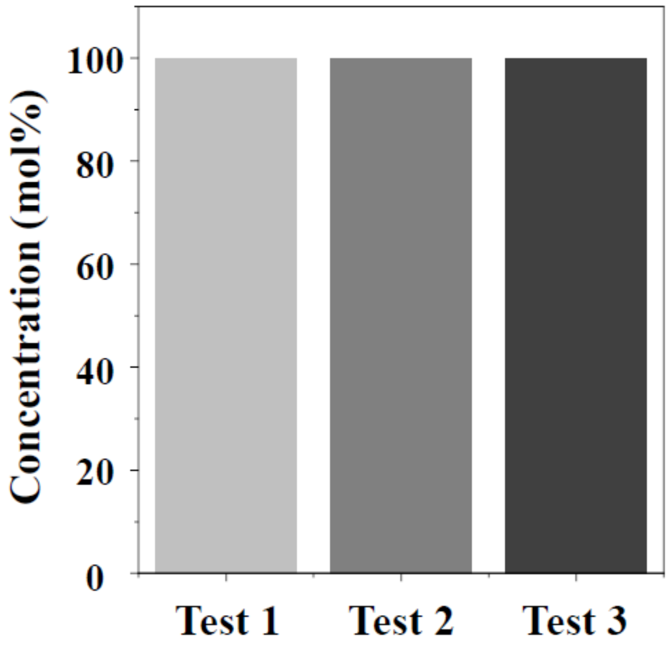


Hydrogenation of styrene



- ***Mild reaction temperature***
- ***Low hydrogen pressure***

Catalytic activity



Styrene: 2 mmol
Catalyst: 20 mg
Reaction temperature: 80 °C

- 5~60 psig H_2
- Reaction time: 24 h

Future directions?

- Improvement of hydrogenation
  - Milder conditions
  - Thermal approach
- A package of additives
  - Other components from biomass or waste
- Scale up

Image courtesy of https://ecampusontario.pressbooks.pub/healthdiseasetopics/chapter/7-5-future-directions/

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